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XANES Analysis Of Adsorbed Phosphate Distribution Between Ferrihydrite and Boehmite in Mixed-Mineral Systems

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Introduction: Runoff and drainage waters containing excessive levels of soil P may cause deterioration of surface water quality. Iron and Al-oxide minerals are important sorbents for retaining inorganic phosphate in soils. The relative distribution of phosphate between Fe- and Al-oxide minerals may affect its dissolution from soils. Our objective was to determine the relative distribution of adsorbed phosphate between poorly crystalline analogues of Fe – oxide (ferrihydrite) and Al-oxide (boehmite) in aqueous mixtures.

Methods and Materials: Phosphate was adsorbed at concentrations up to 1900 mmol/kg in aqueous suspensions containing ferrihydrite, boehmite, or a 1:1 (by mass) mixture of these minerals at pH 6.

Results: The adsorption isotherm for the mixed-mineral suspensions could be fit as a linear combination of isotherms for each single-mineral suspension, indicating no mineral interactive effects on PO_4 adsorption in the mixed suspensions. Phosphorus K-XANES spectra exhibited no systematic changes with adsorbed PO_4 concentration. XANES spectra for PO_4 adsorbed on ferrihydrite had a pre-edge feature at ~2146 eV that was absent in the spectra for PO_4 adsorbed on boehmite. XANES spectra of phosphate adsorbed in ferrihydrite/boehmite mixtures showed a trend of decreasing intensity of this pre-edge feature with increase in adsorbed concentration. Linear combination fitting of the pre-edge region with average spectrums for PO_4 adsorbed on boehmite or ferrihydrite at different levels gave a quantitative assessment of the quantities of PO_4 adsorbed on each mineral in the mixed systems. For adsorbed concentrations up to 400 mmol PO_4/kg, XANES fitting indicated that 72 to 100% of the PO_4 was adsorbed on ferrihydrite. For concentrations between 400 and 1300 mmol PO_4/kg, 66 to 48% of added PO_4 was adsorbed on ferrihydrite. Because ferrihydrite had 2.2 times greater maximum PO_4 adsorption (1860 mmol/kg) compared with boehmite (850 mmol/kg) relative distribution of PO_4 between ferrihydrite and boehmite obtained from the fitting results were normalized by dividing with the maximum PO_4 adsorption capacities of these minerals. A comparison of the PO_4 distribution between the two minerals based on XANES results and the predicted amount of PO_4 on each mineral assuming adsorption in proportion to each mineral's maximum adsorption capacity (no affinity preference), showed that boehmite had a slightly greater affinity for PO_4 at adsorbed levels greater than 400 mmol/kg.

Conclusions: Phosphorus K-XANES analysis of o-phosphate adsorbed in aqueous, mixed Fe-/Al-oxide mineral suspensions showed that the amount of adsorption to each mineral was nearly proportional to the relative PO_4 adsorption capacity of each mineral in the system, with some preference for PO_4 shown by boehmite at higher concentrations.

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